A STUDY OF GAS SOLUBILITIES AND TRANSPORT PROPERTIES
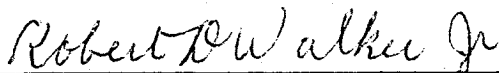IN FUEL CELL ELECTROLYTES

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# 1. Summary

This report deals with apparatus for measuring vapor pressures of $KOH-K_2CO_3$ solutions, diffusivities of oxygen in lithium hydroxide solutions, an apparatus for making more accurate measurements of gas solubility in KOH solutions, and an analysis of some problems in measuring heats of solution of gases in electrolytes.

The differential manometer which has been used in earlier measurements of the vapor pressure over $KOH-K_2CO_3$ solutions is limited as to the upper temperature at which it can be used. This equipment has been redesigned to make possible vapor pressure measurements up to about 150°C. It is currently being tested for leaks and for high temperature operation.

Diffusion coefficients of oxygen in lithium hydroxide have been made with a stagnant microelectrode up to LiOH saturation and to a maximum temperature of 80°C. These experimental values differed from those measured with the dropping mercury electrode by as much as 20%. It appears likely that heat effects due to the mercury drop being at a different temperature than the solution so disturbs the boundary layer that significant errors are introduced in the diffusion coefficients derived from the limiting current measurements.

An improved apparatus for measuring gas solubilities in concentrated electrolytes has been designed. It relies on air lift principle to provide both saturated and solution circulation. Flow control is exercised by means of solenoid valves. It is anticipated that substantially greater accuracy in gas solubility measurements can be obtained with this equipment.

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An analysis of the rate of heat generation on the dissolution of sparingly soluble gas in electrolytes has been made, and it leads to the conclusion that the temperature changes to be expected are much too small to be measured with precision owing to the slowness of the gas dissolution. It appears that more accurate gas solubility measurements are the only real hope of improved precision in heats of solution and other thermodynamic properties.

## 2. Vapor Pressure of KOH-K$_2$CO$_3$ Solutions

The vapor pressure of aqueous KOH-K$_2$CO$_3$ solutions has been measured over a considerable concentration range and at temperatures up to 80°C using a differential manometric method, and these results were reported in the last semi-annual report (#11). The vapor pressures were correlated quite well by equations and procedures developed and presented in that report. It appears desirable to extend the range of conditions covered in the former work; however, certain problems with the earlier apparatus have required its redesign, particularly for its operation at higher temperatures.

### 2.1 Apparatus

The apparatus is as shown in Figure 1. The former differential manometer has been modified so as to connect a vacuum pump to the sample containers. Since at high temperature KOH corrodes glass, two nickel flasks with threaded joints are used for the sample and reference solutions. Flasks A and B are connected to the side arms of the manometer using stainless steel Cajon fittings. A three 3-way valve (C) connects the flasks to a vacuum pump which serves to remove the dissolved gases from the solutions and to remove all traces of air from the vapor space.

The manometer employs a stainless steel needle (F) connected to a micrometer (D) to measure the height of the mercury column (I). The micrometer is readable to 0.0005" (approximately 0.01 mm). To isolate the micrometer from high temperature bath an extension tube (K)
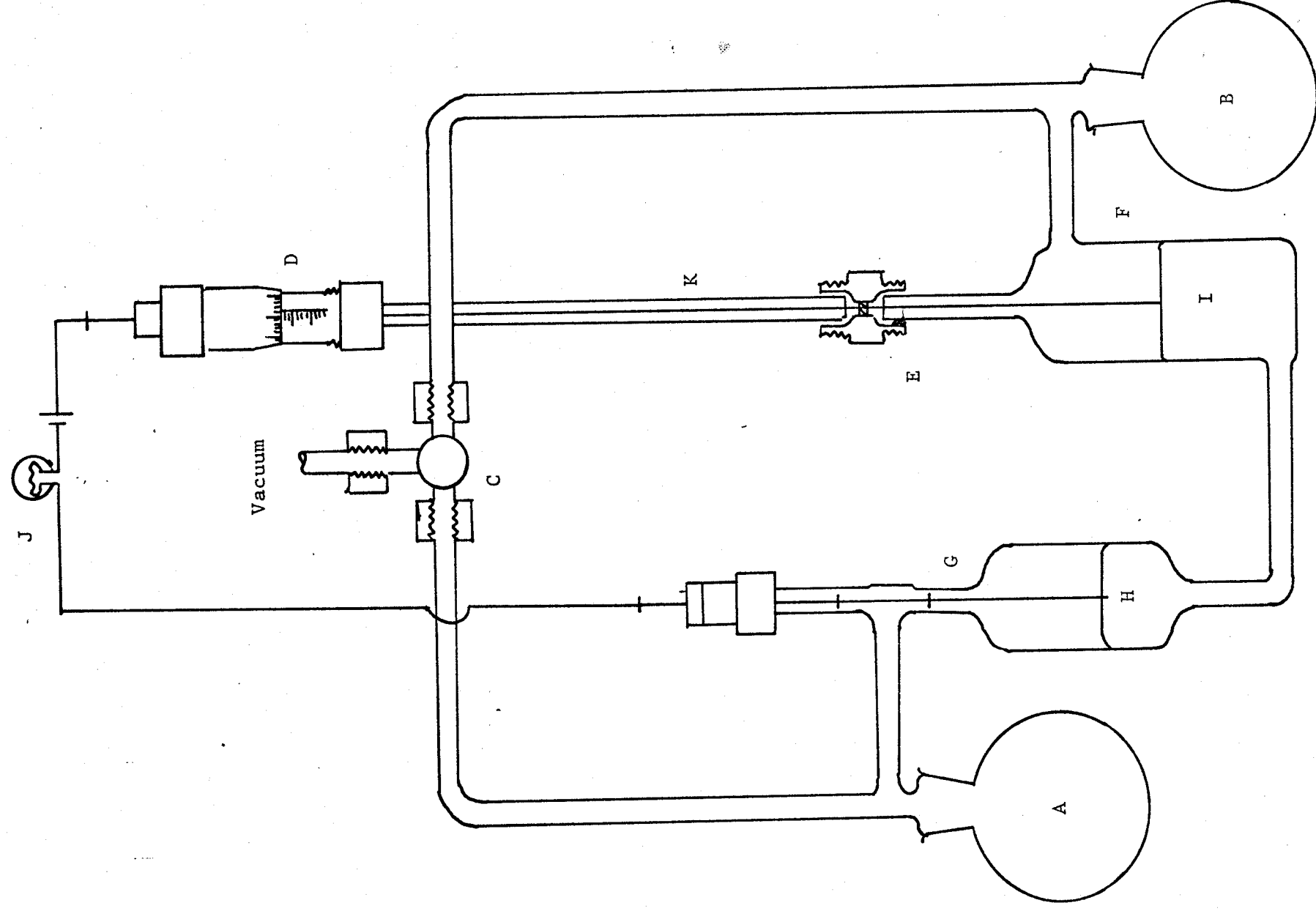
Figure 1. Schematic Diagram of Differential Manometer.

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is joined to the manometer tube by means of a stainless steel Cajon union. A chromatographic silicone septum (E) is embedded in the Cajon fitting in order to prevent vapors from entering the extension tube (K) where condensation could take place.

The problem of scum deposits on the mercury surface made accurate visual sighting difficult. Therefore, measurements are being made by electrical contacts rather than by visual means. To achieve this the needle F is taken all the way through micrometer D and another needle (G) is sealed in the other arm of the manometer in such a way that it always remains dipped into the pool of mercury (H). These two needles are connected electrically using a dry cell. A light bulb (J) in this circuit acts as an indicator--glowing when needle F just touches mercury column I.

## 2.2 Constant Temperature Bath

Use of Nujol oil, instead of water, in the constant temperature bath extends the range up to 140° - 150°C. However, even up to this temperature, Nujol is inconvenient to use due to excessive evaporation and condensation on surrounding laboratory equipment. Also, over an extended period at such temperatures the oil becomes dark and thick.

Design of a vapor bath is in progress. A stainless steel pressure vessel, shown in Figure 2, houses the manometric assembly described above. The cover of the vessel has openings for:

    (i)     vacuum line

    (ii)    extension tube for micrometer
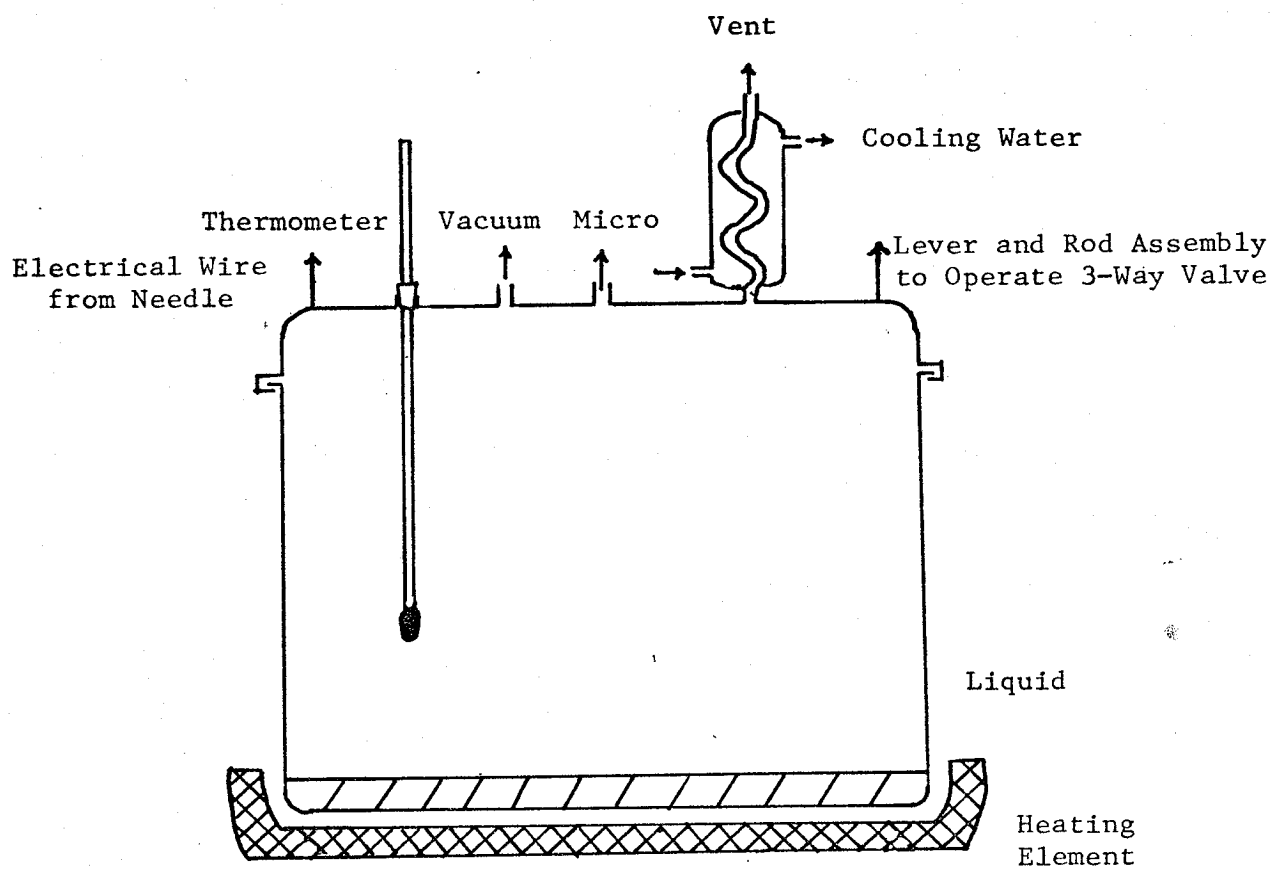
    (iii)   electrical wire from needle (G)

Figure 2.   Schematic Diagram of Vapor Thermostat.

(iv)     thermometer

(v)      condenser

(vi)     lever and rod assembly to operate 3-way valve.

The cover is attached to the main body by a bayonet mount.  A Teflon

gasket is used to seal the vessel.  Noncorrosive organic liquid

boiling at atmospheric pressure should maintain the temperature at

its boiling point.  A water cooled condenser located on top of the

vessel returns the liquid to the vessel.

## 2.3  Choice of Standard Solutions

In the previous work distilled water was used as standard at

low temperatures and low concentrations (1).  Because of the limited

scale of the micrometer (approximately 50 mm) many of the samples at

higher temperatures were run against previously established standards

rather than water.

To avoid any possible accumulation of errors an extensive

literature search was made for suitable reference system.  Vapor

pressures of NaCl (2) and KCl (3) are reported over a wide range of

concentration and temperature.  Hence, these solutions are being used

as standards.

## 3. Diffusion Coefficients of Oxygen in Lithium Hydroxide Solution

Diffusion coefficients of oxygen in lithium hydroxide solutions at 25°C, 40° and 60°C have been measured using the dropping mercury electrode (4). In the present work these coefficients were measured using the stagnant microelectrode method. In addition, a few measurements at 80°C were made.

### 3.1 Experimental Technique

The stagnant microelectrode method of measuring diffusion coefficients is based on electrochemical reduction or oxidation of the diffusing system at the platinum electrode which is placed at the end of a capillary. This reaction induces a known low gas concentration (generally zero) at the electrode, and a high gas concentration is maintained (generally saturated) at the other end of the capillary, thus allowing the diffusion equation to be solved and diffusion coefficient calculated. The stagnant microelectrode method of measuring diffusion coefficient was first developed by Laitinen and Kolthoff (5), and subsequently has been used by many others (6,7). Detailed descriptions of the apparatus and subsequent changes have been reported previously (7,10) and will not be repeated here.

### 3.2 Experimental Results

The measured diffusion coefficients are plotted in Figure 3, and tabulated in Table 1. Also plotted are data obtained earlier by means of the dropping mercury electrode (4). There are differences in the two methods, both in the absolute magnitude and the trend of variation of

## TABLE 1

### DIFFUSION COEFFICIENTS OF OXYGEN IN LITHIUM HYDROXIDE SOLUTIONS

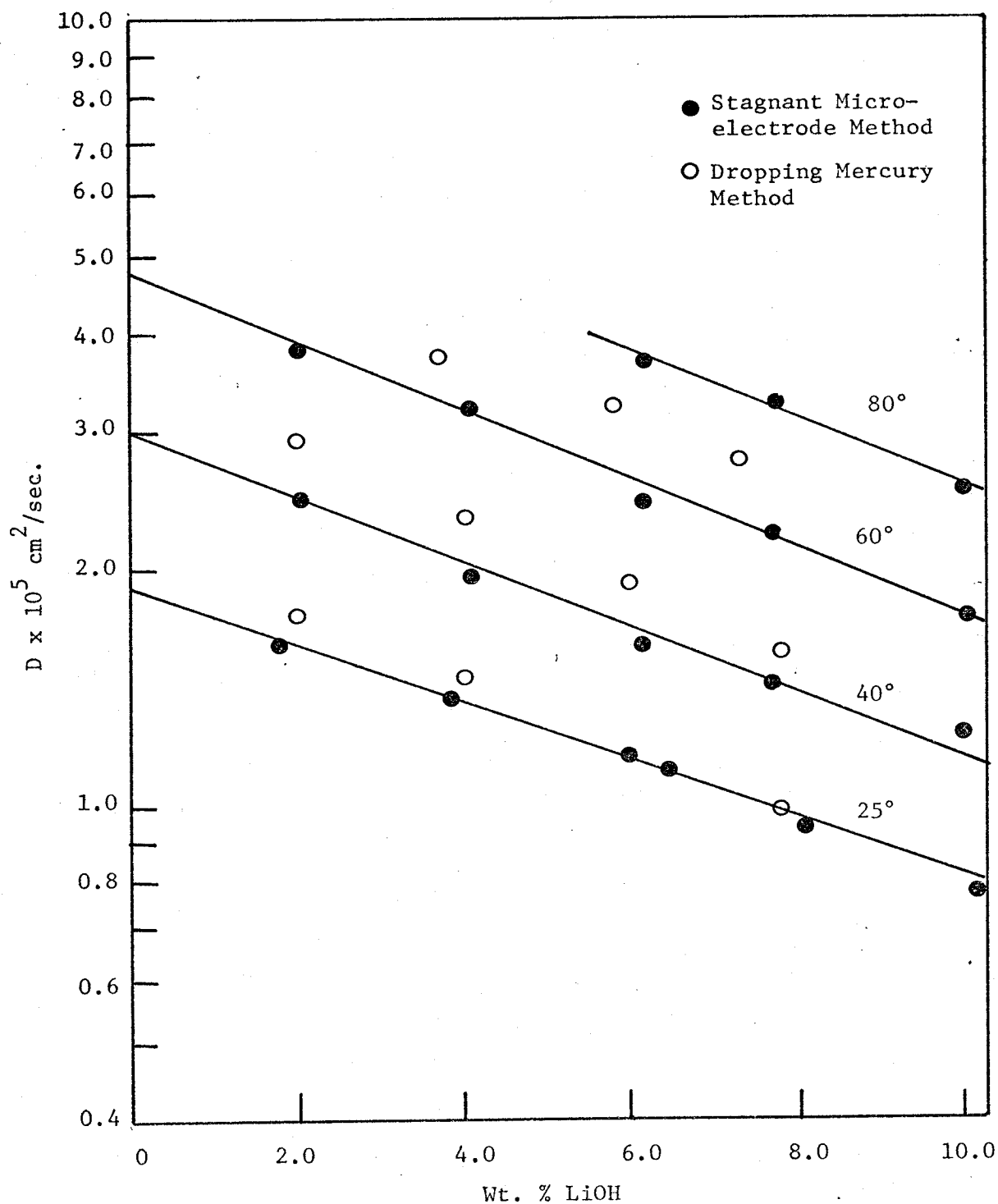| Wt. % LiOH | 25° | 40° | 60° | 80° |
|---|---|---|---|---|
| 1.90 | 1.60 | | | |
| 2.06 | | 2.48 | 3.84 | |
| 3.85 | 1.38 | | | |
| 4.10 | | 1.97 | 3.22 | |
| 6.15 | | 1.74 | 2.44 | 3.76 |
| 6.45 | 1.12 | | | |
| 7.70 | | 1.45 | 2.21 | 2.30 |
| 8.05 | 0.95 | | | |
| 10.05 | | 1.25 | 1.78 | 2.56 |
| 10.10 | 0.79 | | | |

Figure 3. Diffusion Coefficient of $O_2$ in LiOH Solution.

diffusion coefficients with concentration. The differences may be due to temperature fluctuations and effect of viscosity in the dropping mercury electrode method.

At temperatures higher than 80°C the rapid evaporation of the solution made it difficult to do measurements using either the stagnant microelectrode method or the dropping mercury method. In such cases it might be desirable to use either the quasi-steady state (11) or the steady-state diaphragm cell method (12). The use of the bubble method currently being studied in this laboratory (13) might also prove satisfactory for high temperature measurements.

### 3.3   Comparison with Theory

Hard Sphere Kinetic Theory. The hard sphere kinetic theory described in previous reports (10, 14) was used to calculate the diffusion coefficient of oxygen in lithium hydroxde at various temperatures and electrolyte concentrations. The results are plotted in Figure 4, together with the experimental data. The hard sphere theory is not capable of predicting accurately the temperature dependence of the diffusion coefficient. The prediction of concentration dependence is in general good. In order to have the proper temperature dependence, the hard sphere diameters for the different species were calculated from the experimental data at one concentration and used to predict the diffusion coefficients at other concentrations. As can be seen from Figure 4, the theory does predict the correct diffusion coefficients.
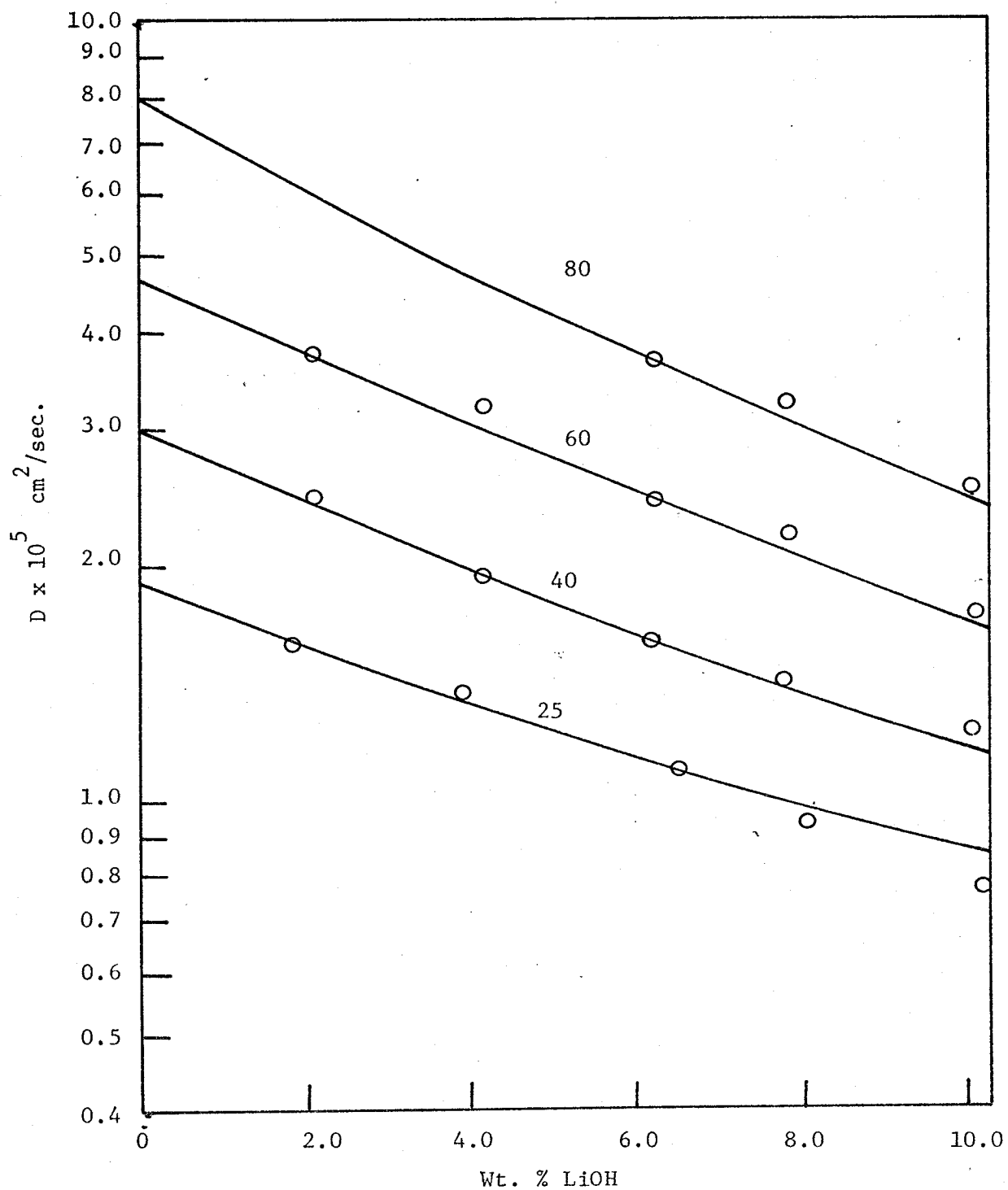
Figure 4. Hard Sphere Kinetic Theory Prediction of Diffusion Coefficient of $O_2$ in LiOH Solution.

Modified Eyring Theory. The modified Eyring theory (10) predicts that the plot of $\ln D/D^o$ against species fraction should be a straight line. These were plotted in Figures 5, 6 and 7 using data obtained in this work. We found that in all cases linear relations were observed. The modified Eyring theory, though capable of predicting the relationship that the diffusion coefficients have with its value at infinite dilution, it is not a predictive theory and thus cannot be considered a complete theory.

Conclusions. The methods used in this laboratory for measuring diffusion coefficients of gases in electrolytes are not suitable for use at temperatures higher than 100°C. Other methods such as bubble dissolution or the steady state diaphragm cell appear to be more suitable for high temperature measurement.

Present theories of diffusion are far from adequate for predictive purposes. The modified Eyring theory is a nonpredictive theory, and can be considered only as an empirical correlation. The hard sphere theory, admittedly a better theory based on statistical mechanics, cannot predict the temperature dependence of diffusion coefficient due to the nature of the hard sphere model. A more realistic model will require solving the many-body problem. At the present time it is not possible to solve both from the equilibrium and transport theory point of view.
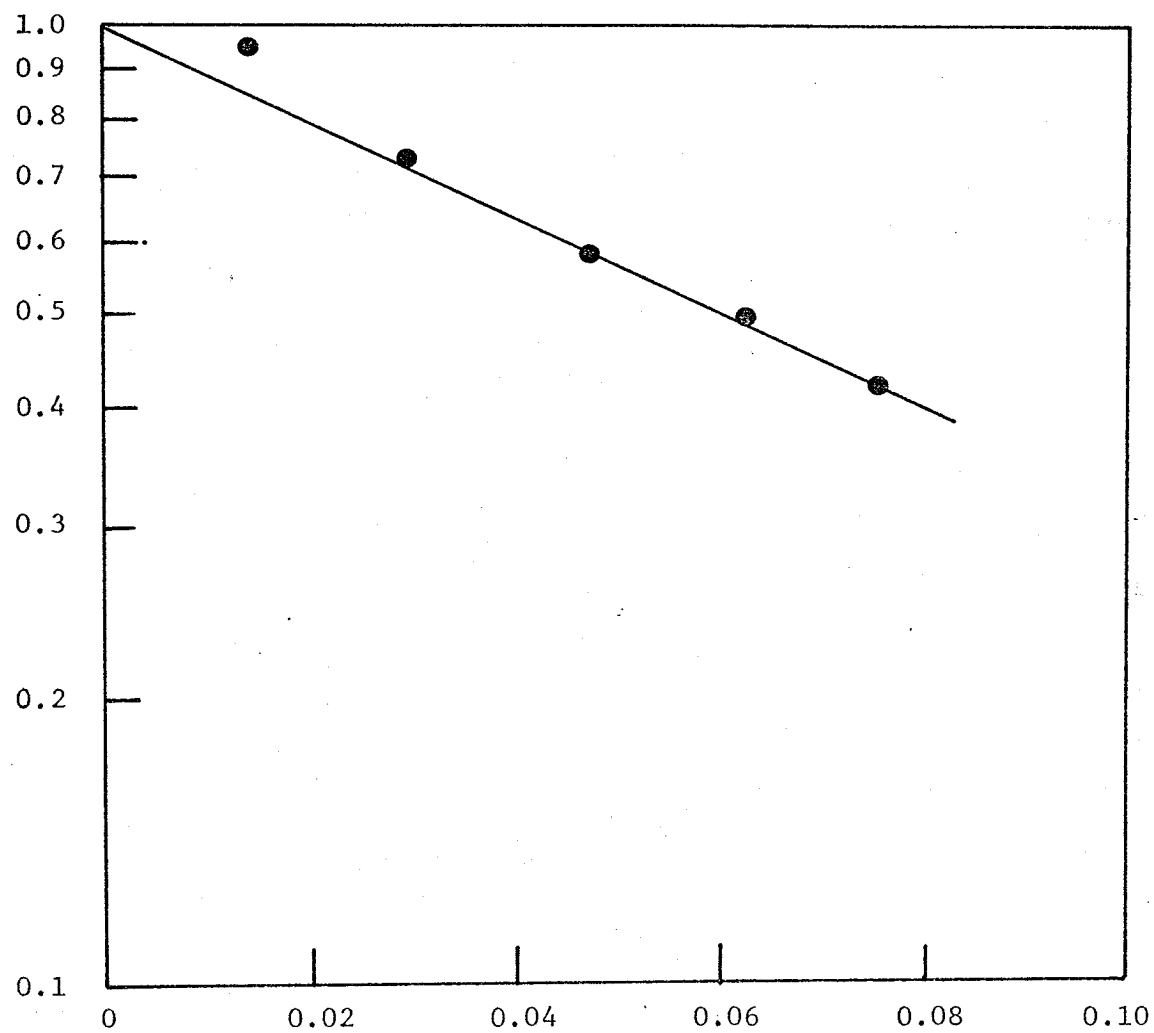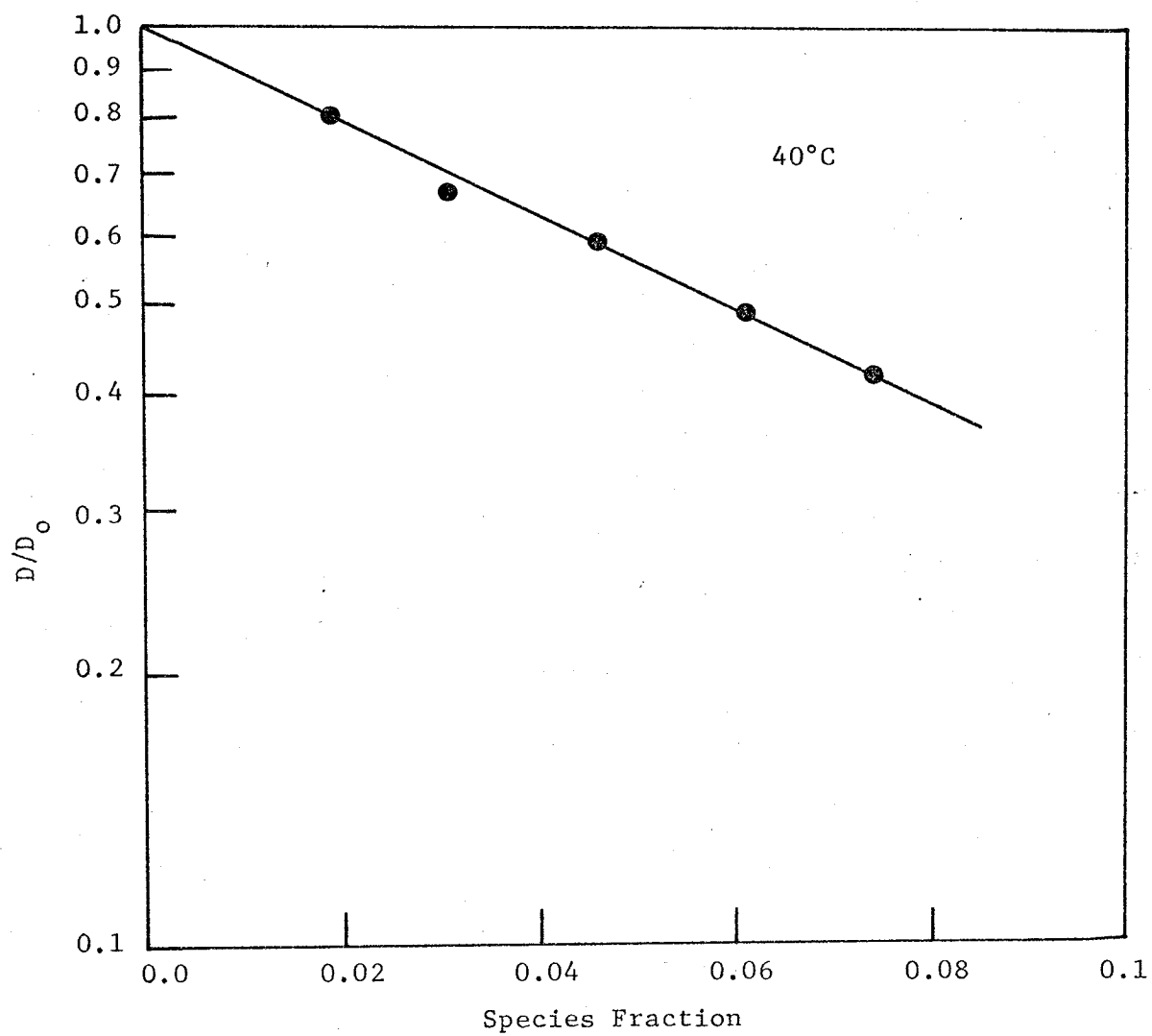
Figure 5.  lnD/D$_o$ vs. Species Fraction at 25°C.
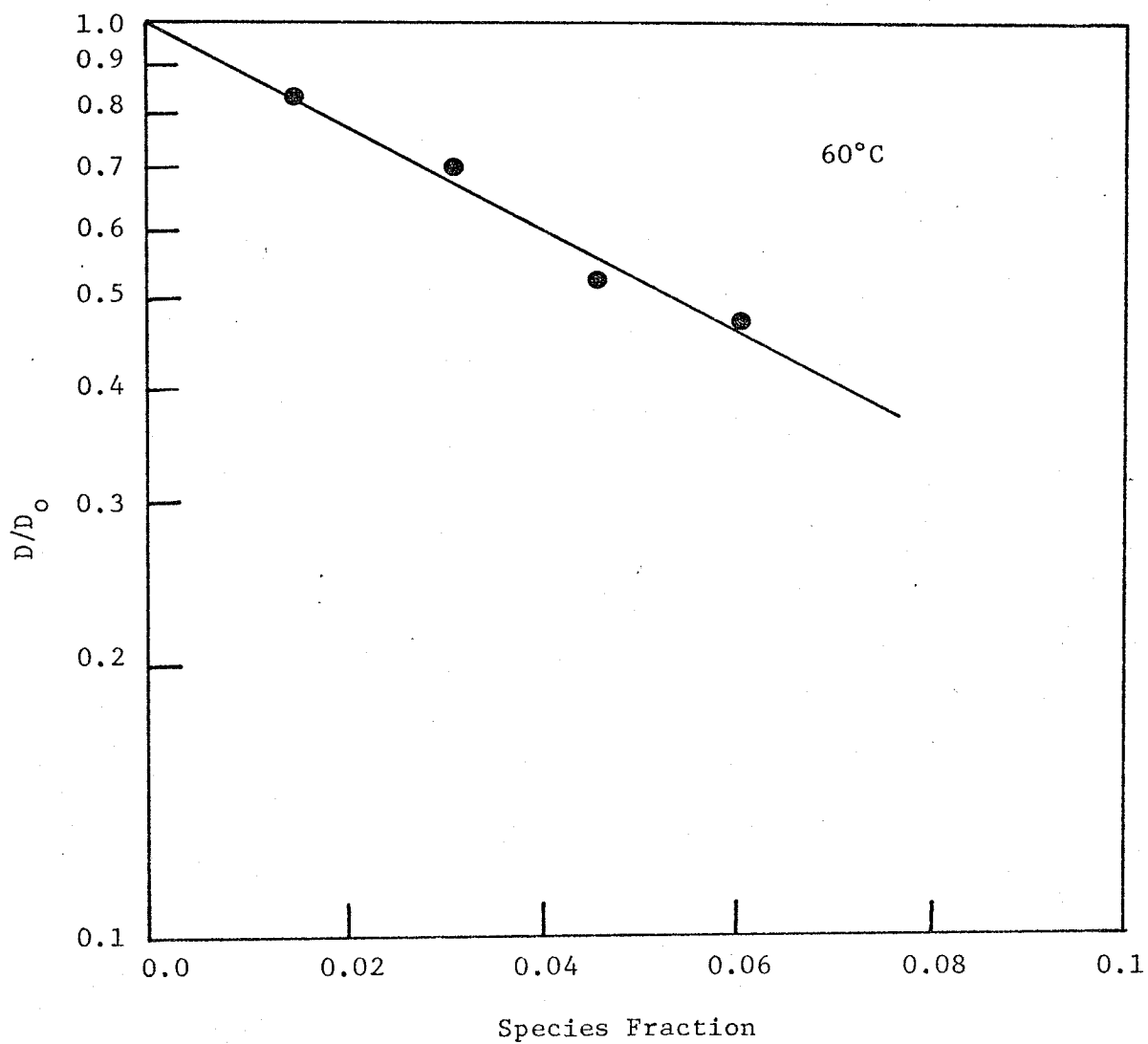
Figure 6. $\ln D/D_o$ vs. Species Fraction at 40°C.

Figure 7. lnD/D$_o$ vs. Species Fraction at 60°C.

## 4. Improved Solubility Apparatus and Experimental Procedure

The saturation assembly shown in Figure 8 is, at present, constructed out of glass and consists of two 15 cc and 30 cc bulbs with appropriate side arms. However, it is anticipated that the final design will call for nickel or stainless steel as a material of construction to avoid corrosion at high temperatures and high concentrations of KOH. This unit is connected to the chromatograph by means of stainless steel tubing. Three 3-way solenoid valves made of stainless steel and designed to withstand high temperatures (200°C) are used in the line. The entire system is shown schematically in Figure 9.

All three solenoid valves are connected in such a manner that, when deactivated, they permit the fluid to flow in the direction shown by solid arrows. All three solenoid valves are simultaneously energized by a single switch and when energized they allow flow in the direction of broken arrows. Part of the assembly, shown in a rectangular section, is housed in a constant temperature bath. In order to make equilibrium solubility measurements at high temperatures a vapor bath, similar to the one described in Section 2, is in the design stage.

### 4.1 Saturation of Solution with Gases

Initially with the solenoid valves in the deactivated position, a solvent liquid is charged through inlet tube (A) equipped with a funnel and a stopcock. The solute gas is bubbled through a set of presaturators containing the same solution as that being studied. The presaturators are required to saturate the gas with water vapors so as
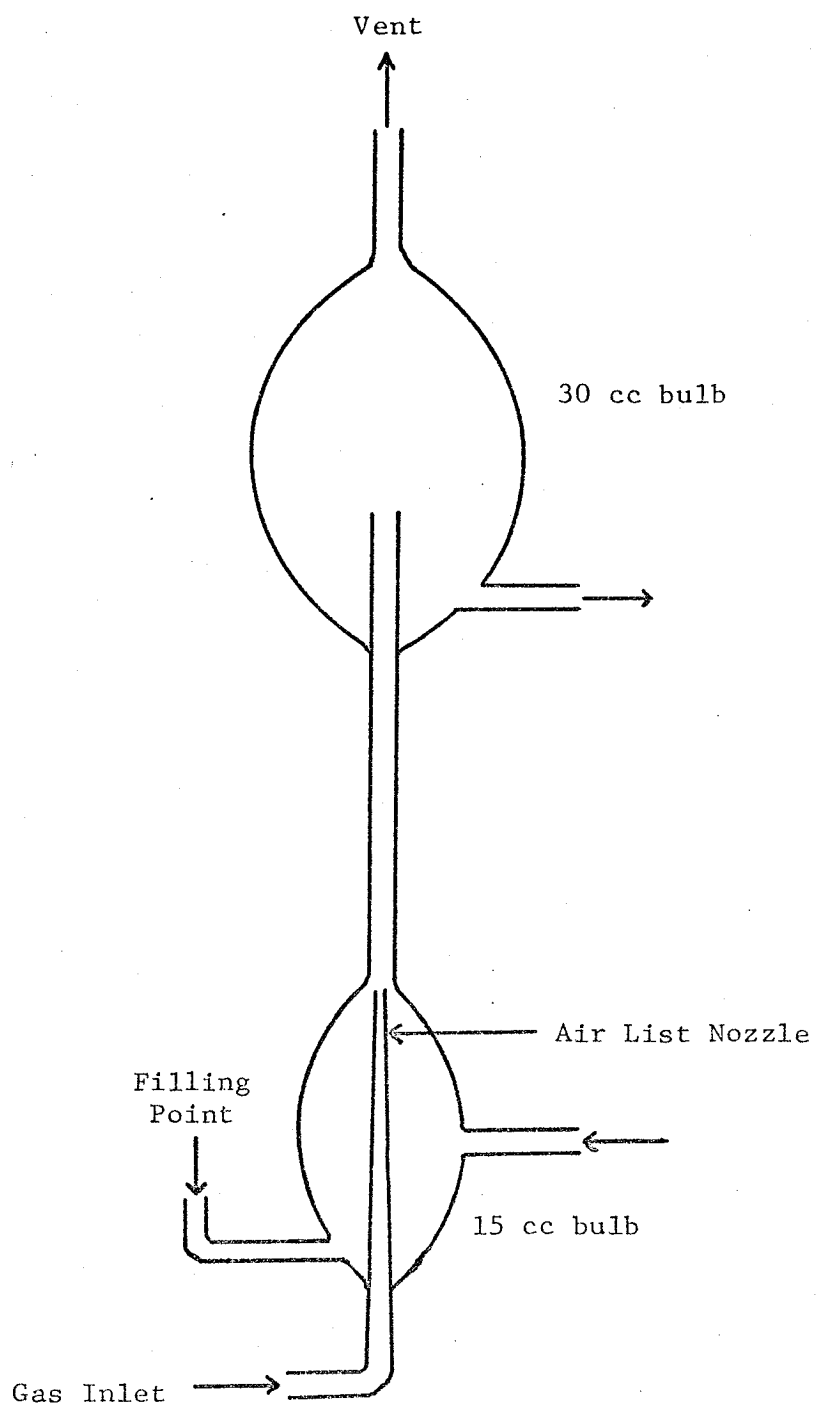
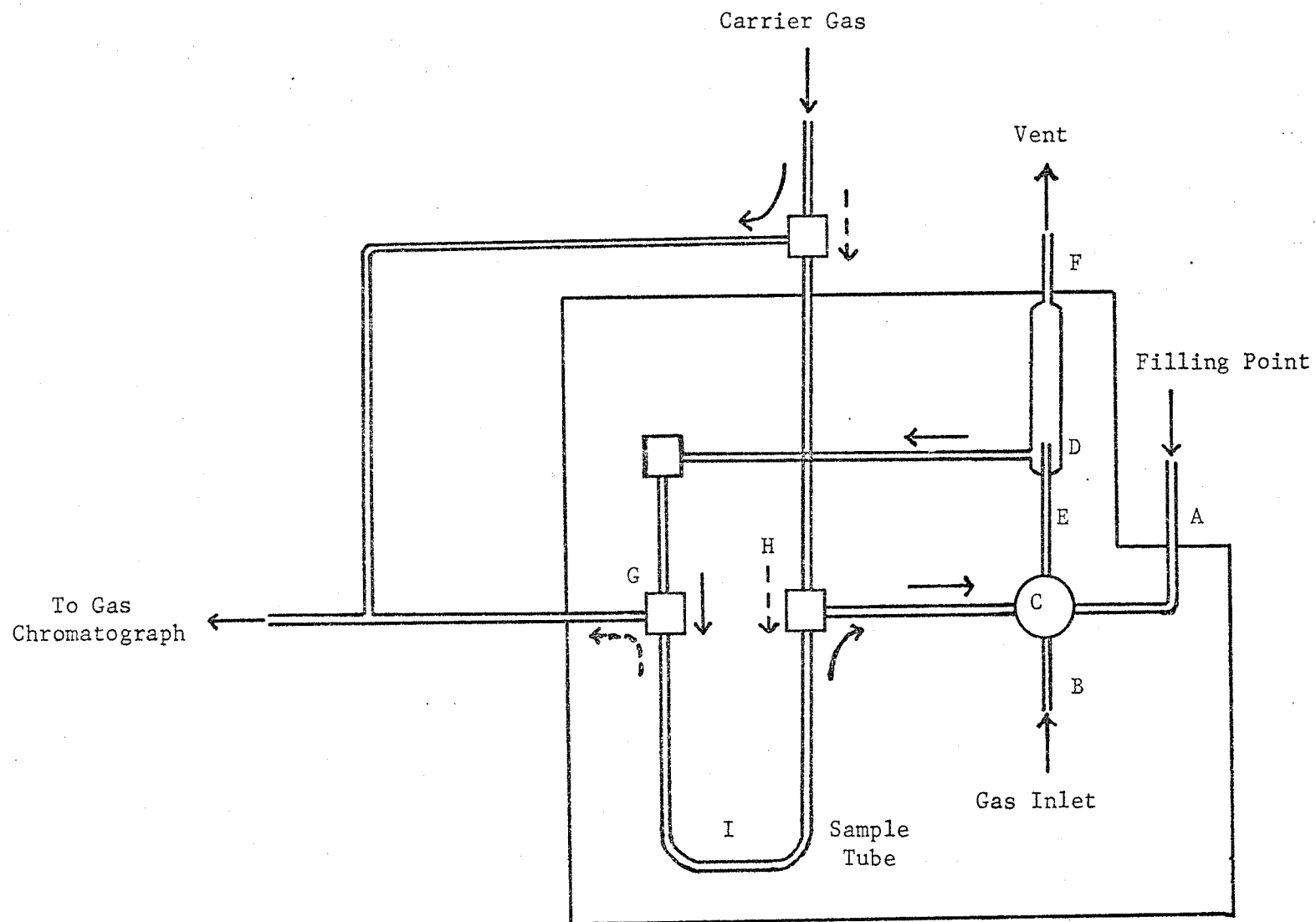Figure 8.   Schematic Diagram of the Saturation Device.

Figure 9.  Schematic Diagram of Solubility Cell.

not to change the concentration of the solution under test. This

saturated gas is then bubbled through the nozzle inlet B. The gas

bubbles in lower bulb C lift the solution to upper bulb D via tube E.

The carrier tube is sealed into the upper bulb with its height so

adjusted as to effectively separate gas and liquid phases. The

undissolved gas escapes through a vent F. The solution containing

dissolved gas collects in the bottom of the upper bulb and travels in

the direction of the solid arrows through solenoid valves G and H, and

a calibrated sample tube I; thence it returns to the lower bulb C.

The liquid outlet of the upper bulb and inlet to the lower bulb

are joined at the lowest possible point in order to minimize any

stagnation of the solution.

The process is continued until equilibrium is attained. It

is believed that, due to very good gas liquid contact during the air

lift, equilibrium should be attained rapidly. Attainment of equilibrium

is of prime importance for equilibrium solubility determinations and

this is checked by withdrawing samples after different intervals of

saturation time and analyzing for the dissolved gas. It is concluded

that equilibrium has been attained when at least 3 samples withdrawn

at different times give the same result within the limits of experimental

error.

## 4.2 Sampling and Analysis

When the solenoid valves are energized, carrier gas flows

through the system in the path shown by broken arrows, sweeping out

the liquid sample from the sample tube I. The sample tube is of

previously calibrated volume. Calibration is done either
gravimetrically by weighing the tube empty and when filled with mercury
or chromatographically by passing a gas through the system with
deactivated solenoid valves and then energizing the solenoid valves
to sweep the gas sample into the chromatograph. For those gases
where accurate solubility values in water at 25°C were available in
the literature, the calibration is checked by carrying out the experi-
ment on water sample.

This known volume of saturated solution is emptied in a glass
stripping column similar to one used previously (15). The carrier
gas strips the dissolved gas from the solution, carries it through a
glass tube filled with Drierite to remove water vapor and into the
chromatograph column. Analysis is made using a thermal conductivity
detector. Helium is used as the carrier gas. The chromatograph is
calibrated by injecting an accurately measured volume of pure dry gas
and measuring the area of the resulting peak.

## 5. Heat of Solution of Gases in Electrolyte Solutions

In Chemical Engineering process design and optimization, the need for heat of solution data usually occur along with such data as heat capacity and heats of reaction. The values of the heat of solution range from a few calories per mole for chemically similar mixtures, to several thousand calories per mole for chemically different solutions. The technique used for each kind of mixture will be different in each case.

In general the sources of heat of solution data can be divided into two categories. Those obtained through direct calorimetric measurement and those through solubility studies.

### 5.1 Calorimetric Methods

The use of calorimetric methods to measure the heat generated in a physical or chemical process is a relatively common practice. Its application in the accurate measurement if the heat of solution of liquids is, however, a relatively recent happening. It is only recently that measurements of heat of solution have attained the degree of precision needed for significant test of theories of solution (16). Reviews by McGlashan (17), and Rowlinson (18) also pointed out that agreement between any two laboratories has been exceptional enough to require special comment. Rapid development in experimental techniques and better electronic set-up has improved the situation significantly, and better agreements were achieved by workers in this field.

The methods of measuring heat of solution of liquids can be classified into (1) flow calorimetry, (2) batch calorimetry.

Flow Calorimeter. This method is a recent development, and has been widely used for use in liquid systems (19, 20, 21). This design has certain features which make it ideal for work with liquid systems. It has high calorimetry sensitivity, complete absence of any vapor phase, without the use of cumbersome filling and separating agents. The fluid handling system can be constructed entirely of glass, Teflon and stainless steel, so that corrosion will not be a significant problem.

The flow calorimeter is usually run at steady-state conditions, and the lack of moving parts has made it more easily adapted in a differential mode.

On the whole, this method is reliable and accurate for liquid systems. Unfortunately, this method cannot be used when there are two phases present. The transport of material between the two phases complicates the process, and the measured heat effect will include such heats as turbulent heat dissipation, evaporation, and other heats generated by various transport processes in addition to the heat of solution we are interested in measuring.

Batch Calorimeter. Most of the research in heat of solution of liquids has been carried out in batch calorimeter (22, 23, 24). This is based on the mixing of two liquids which were separated by a mercury layer (23, 25) or a diaphragm (26). Mixing is facilitated by breaking these seals. Another variation of this is by introducing the liquid by means of a syringe (16, 27, 28). Corrections were made for any mechanical heat that might be generated. To enhance mixing a stirrer is sometimes used. To compensate for mechanical heat and

the heat equivalent of the vessel the differential mode was also used

(24). Even though batch calorimeters are less effective than the flow

calorimeters, it is the only type which can be reasonably readily

adapted for gas-liquid systems. Vanderzee et al. (29, 30) used a

batch micrometer for measuring heat of solution of HF, HBr and HCl

in water.

The sensitivity of most calorimeters is in the range of $10^{-5}$°K.

Heat effects of $10^{-3}$°K can be measured with an accuracy of one percent

or better. Heat generated in the dissolution of $H_2$ and $O_2$ in KOH

solutions is sufficient to cause temperature changes in the range of

$5 \times 10^{-3}$ to $5 \times 10^{-5}$°K, which is within the range of measurability

of the present techniques. Unfortunately, whereas the above mentioned

heat effects are those generated instantaneously (reaction of HCl with

NaOH, for example), this is not so for the case of dissolution of gases

in electrolyte. The dissolution process may take any where from

several hours to several days (31), thus spreading the heat generated

over a length of time so long that the measured temperature change will

be several orders of magnitude lower than the achieved sensitivity at

the present moment. This slow process of dissolution of gases in

electrolyte excludes the possibility of using calorimetric methods

for measuring its heat of solution.

## 5.2 Heats of Solution Through Solubility Measurement

All of the heat of solution data we have reported were obtained

through solubility measurements (32, 33). A computer study using

randomly generated errors shows that the calculated heat of solution

will be less than 5% in error if the error in solubility measurement is kept within 2%. Analysis of the possible errors in the measurement of solubility data using chromatographic methods reveals that maximum errors can be introduced in the following steps:

    (1)   saturation process

    (2)   temperature control

    (3)   handling of liquid before chromatographic analysis.

In order to eliminate these possible errors, a solubility cell has been designed to ensure proper saturation and minimize handling of liquids (see Section 4).

## References

1. Walker, R. D., Jr., Eleventh Semi-Annual Report, June 17, 1971, NASA Research Grant NGL 10-005-022.

2. Smith, R. P., J. Am. Chem. Soc., 61, 500 (1969).

3. Smith, R. P. and D. S. Hirtle, J. Am. Chem. Soc. 61, 1123 (1969).

4. Walker, R. D., Tenth Semi-Annual Report, Oct., 1970, NASA Research Grant NGR 10-005-022.

5. Laitinen, H. A., and Kolthoff, I. M., J. Am. Chem. Soc., 61, 3344 (1939).

6. Von Stackelberg, M., Pilgrim, M., and Toome, V., Z. Electrochem., 57, 342 (1953).

7. Walker, R. D., Sixth Semi-Annual Report, Feb., 1969, NASA Research Grant NGR 10-005-022.

8. Tham, M. K., Walker, R. D., and Gubbins, K. E., J. Phys. Chem. 74, 1747 (1970).

9. Kolthoff, I. M. and Lingane, J. J., "Polarography," Vol. I, Interscience, New York (1952).

10. Walker, R. D., Eleventh Semi-Annual Report, June, 1971, NASA Research Grant NGR 10-005-022.

11. Bhatia, R. N., M.S.E. Thesis, University of Florida (1967).

12. Tham, M. J., Bhatia, K. K., and Gubbins, K. E., Chem. Eng. Sci., 22, 309 (1967).

13. Jalan, V. M., Private Communication.

14. Tham, M. K., and Gubbins, K. E., Technical Paper Presented at A.I.Ch.E. Meeting, August, 1970, Denver, Colorado.

15. Walker, R. D., First Semi-Annual Report, March 15, 1966, NASA Research Grant 10-005-022.

16. Stokes, R. H., Marsh, K. N., and Tomlins, R. P., J. Chem. Thermod., 1, 211 (1969).

17. McGlashan, M. L., "Experimental Thermochemistry," Vol. II, Skinner, H. A., Editor, Interscience, N.Y., 1962.

18. Rowlinson, J. S., "Liquids and Liquid Mixtures," Butterworth, London, 1969.

19. Sturtevant, J. M. and Lyons, P. A., J. Chem. Thermod. 1, 201 (1969).

20. Stoesser, P. R., and Gill, S. J., Rev. Sci. Inst., 38, 422 (1967).

21. Picker, P., Jolicoenr, C. and Desnoyers, J. E., J. Chem. Thermod., 1, 469 (1969).

22. Sturtevant, J. M., "Techniques of Organic Chemistry," Vol. 1, Weissberger, A., Editor, Interscience, N.Y., 1959.

23. Wilhoit, R. C., J. Chem. Ed., 44, A571, A685, A853 (1967).

24. Picker, P., Jolicoeur, C. and Desnoyers, J. E., Rev. Sci. Instrum., 39, 676 (1968).

25. Watts, H., Clarke, E. C. W., and Glen, D. N., Can. J. Chem. 46, 815 (1968).

26. Bennett, J. E., and Benson, G. C., Can. J. Chem., 43(7), 1912 (1965).

27. Ewing, M. B., Marsh, K. N., Stokes, R. H. and Tuxford, C. W., J. Chem. Thermodynamics 2, 751 (1970).

28. Savini, C. G., Winterhalter, D. R., Kovach, L. H. and Van Ness, H. C., J. Chem. Eng. Data, 11, 40 (1966).

29. Vanderzee, C. E. and Rodenburg, W. Wm., J. Chem. Thermodynamics, 3, 267 (1971).

30. Vanderzee, C. E. and Nutter, J. D., J. Phys. Chem. 67, 2521 (1963).

31. Tiepel, E. W., Ph.D. Dissertation, University of Florida, 1971.

32. Shoor, S. K., Ph.D. Dissertation, University of Florida, 1968.

33. Battino, R. and Clever, H. L., Chem. Rev. 66, 395 (1966).